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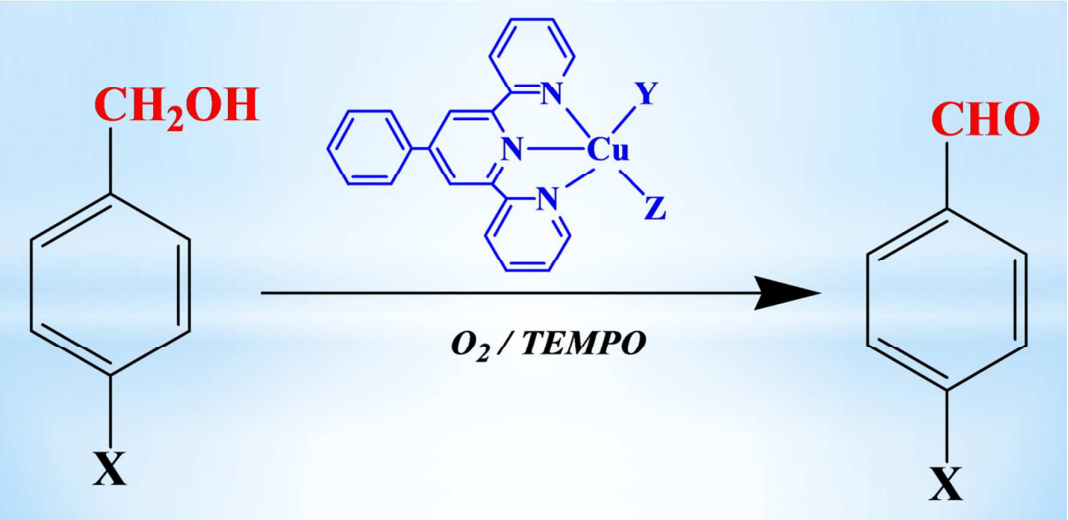
Graphical Abstract



Cu(II)-terpyridine complexes in combination with TEMPO exhibit catalytic activity, under mild conditions and in alkaline aqueous solution, for the aerobic oxidation of benzylic alcohols.

Synthesis and Characterization of Copper(II) 4'-phenyl-terpyridine Compounds and Catalytic Application for Aerobic Oxidation of Benzylic Alcohols

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Abstract

The reactions between 4'-phenyl-terpyridine (L) and nitrate, acetate or chloride Cu(II) salts led to the formation of $[Cu(NO_3)_2L]$ (**1**), **[**$Cu(OCOCH_3)_2L]\cdot CH_2Cl_2$ (**2**$\cdot CH_2Cl_2$) and $[CuCl_2L].[Cu(Cl)(\mu\text{-}Cl)L]_2$ (**3**), respectively. Upon dissolving **1** in mixtures of DMSO/MeOH or EtOH/DMF the compounds $[Cu(H_2O)\{OS(CH_3)_2\}L](NO_3)_2$ (**4**) or $[Cu(HO)(CH_3CH_2OH)L](NO_3)$ (**5**) were obtained, in this order. Reaction of **3** with $AgSO_3CF_3$ led to $[CuCl(OSO_2CF_3)L]$ (**6**). The compounds were characterized by ESI-MS, IR, elemental analysis, electrochemical techniques and, for **2-6**, also by single crystal X-ray diffraction. They undergo, by cyclic voltammetry, two single-electron irreversible reductions assigned to Cu(II) → Cu(I) and Cu(I) → Cu(0), and, for those of the same

structural type, the reduction potential appears to correlate with the summation of the values of the Lever electrochemical E_L ligand parameter, what is reported for the first time for copper complexes. Complexes **1-6** in combination with TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxyl radical) can exhibit a high catalytic activity, under mild conditions and in alkaline aqueous solution, for the aerobic oxidation of benzylic alcohols. Molar yields up to 94 % (based on the alcohol) with TON values up to 320 were achieved after 22 h.

Keywords: copper, 4'-phenyl-terpyridine, catalysis, alcohols oxidation, TEMPO, aqueous medium, E_L parameter, X-ray diffraction

1. Introduction

Multi-pyridyl ligands can coordinate to different metal ions and lead to the formation of a variety of complexes [1]. An example of such ligands is 4'-phenyl-terpyridine (L) which is able to bind several transition metals and lead to interesting fluorescence, catalysis or sensorial properties, or even to quite promising tumor-inhibiting activities [2].

The selective oxidation of alcohols to the corresponding aldehydes and ketones has become an important research topic [3] due to the wide application of these products in organic synthesis [4].

The application of TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxyl radical) in combination with transition metal compounds as catalysts for the aerobic oxidation of benzylic and allylic alcohols was started by Semmelhack and co-workers, using a CuCl/TEMPO system [5]. Since then, this stable free radical has been recognized as a mediator or promoter in several organic reactions [6], and has been widely used in the selective oxidation, with a variety of oxidants, of primary alcohols to the corresponding aldehydes and ketones. Owing to economic and environmental reasons, a

growing attention has been paid to the replacement of the traditionally used, though very active, oxidants (chromates, hypochlorite and permanganates among others) [7] in the alcohols oxidation by the environmentally friendly hydrogen peroxide or molecular oxygen (water as by-product). Another typical source of unwanted waste from these reactions is related with the organic solvents normally used; ionic and supercritical fluids (SCFs) are thus becoming popular [8] as reaction media.

Copper(II) complexes with *N*,*N*- and *N*,*O*-ligands in conjunction with TEMPO were found to be efficient catalysts or catalyst precursors for the aerobic oxidation of benzyl alcohol in aqueous media [9]. Other transition metal catalysts, such as Ru [10], Mn/Cu and Mn/Co [11], Cu [12], V/Mo [13] and Fe [14] were also shown to catalyse the selective oxidation of alcohols to the corresponding aldehydes in the presence of a stable nitroxyl radical. In particular, systems based on Cu [9,12,15] metal centres have been successfully explored.

As a continuation of our research line and aiming to achieve novel terpyridine compounds with promising catalytic or biological properties, we managed to prepare and fully characterize the copper(II) complexes $[Cu(NO_3)_2L]$ (**1**), **[**$Cu(OCOCH_3)_2L]\cdot CH_2Cl_2$ (**2**$\cdot CH_2Cl_2$), $[CuCl_2L].[Cu(Cl)(\mu\text{-}Cl)L]_2$ (**3**), $[Cu(H_2O)\{OS(CH_3)_2\}L](NO_3)_2$ (**4**)**,** $[Cu(HO)(CH_3CH_2OH)L](NO_3)$ (**5**), and $[CuCl(SO_3CF_3)L]$ (**6**). Targeting to contribute towards the development of the application of Cu compounds as catalysts and/or catalyst precursors for the oxidation of alcohols to the respective aldehydes, in aqueous medium and with a readily available and environmentally friendly oxidant, we now report the oxidation, by O_2 (air), of benzylic alcohols catalysed by **1**-**6**/TEMPO systems.

2. Results and Discussion

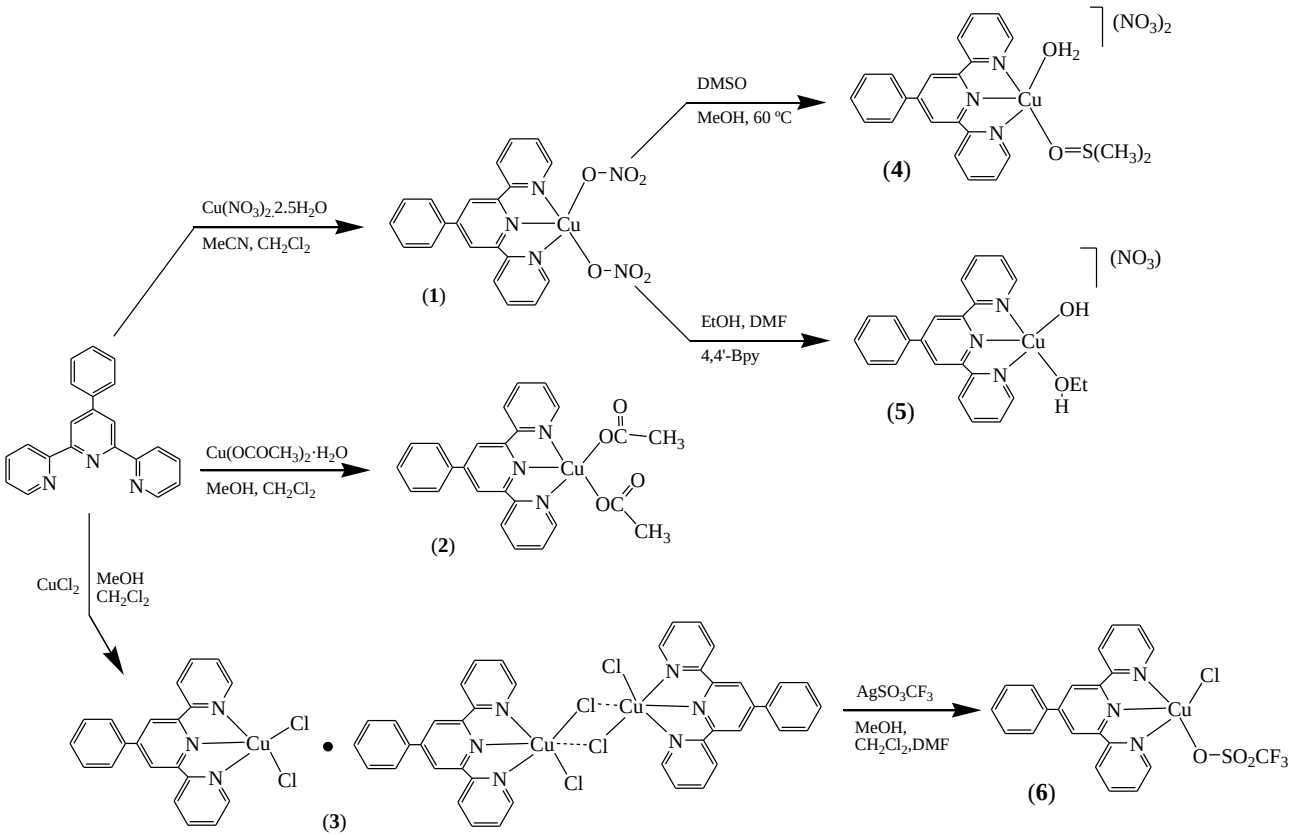
2.1 Synthesis and Characterization

4'-phenyl-terpyridine (L) was synthesized by following a literature procedure [16a], and the copper(II) complexes $[Cu(NO_3)_2L]$ (**1**), **[**$Cu(OCOCH_3)_2L]\cdot CH_2Cl_2$ (**2**$\cdot CH_2Cl_2$), and $[CuCl_2L].[Cu(Cl)(\mu\text{-}Cl)L]_2$ (**3**), were obtained (Scheme 1) by reacting L (added in a CH_2Cl_2 solution) with the appropriate Cu(II) salt, *i.e.* $Cu(NO_3)_2\bullet 2.5H_2O$, $Cu(CH_3COO)_2\cdot H_2O$ or $CuCl_2$, dissolved in acetonitrile (for **1**) or methanol (for **2** and **3**). Compounds $[Cu(H_2O)\{OS(CH_3)_2\}L](NO_3)_2$ (**4**) and $[Cu(HO)(CH_3CH_2OH)L](NO_3)$ (**5**) were obtained upon further reaction of **1** with a methanolic solution of DMSO (**4**) or with 4,4'-bipyridine (4,4'-Bpy) in a DMF:ethanol mixture (**5**). In the latter complex, the OH^- ligand was generated from adventitious water. A similar behaviour was previously reported in the reaction of a trinuclear copper compound with 4,4'-bpy in MeOH, where OH^- displaced an acetate ligand [16b]. In the reaction of **3** with $AgSO_3CF_3$ in NCMe, complex $[CuCl(SO_3CF_3)L]$ (**6**) was obtained. Complexes **1**-**6** were achieved in medium-high yields and characterized by IR, elemental analysis, cyclic voltammetry (CV) and controlled potential electrolysis (CPE), as well as, for **2** – **6**, by single-crystal X-ray diffraction. Although the IR spectra of the compounds were not very informative, they revealed the bands that are typical of the 4'-phenyl-terpyridine, in particular the very strong bands in the 1557 – 1417 cm^{-1} frequency range. The most typical frequency vibrations for nitrate and trifluoromethane sulfonate anions overlay those of the terpyridine ligand. The UV-vis spectra of the compounds run in DMSO are identical to those run in water and reveal their stability in those solvents.

2.2. X-ray crystal structures

Crystals suitable for X-ray diffraction analysis were obtained upon slow diffusion of diethyl ether into a dichloromethane solution (for **2**) or a DMSO:methanol mixture (for **4**), slow evaporation of a

methanol:dichloromethane solution (for **3**) or of the reaction mixtures (for **5** and **6**) (the schematic representations of their formulae are shown in Scheme 1). The ellipsoid plots of complexes **2** – **6** are depicted in Figure 1. Crystallographic data are given in Table 1 and a comparison of selected bonding parameters in Table 2.



Scheme 1 - Syntheses of compounds **1**-**6**

The geometries around the copper ions in complexes **4** – **6** can be considered as rectangular pyramidal, what is supported by the τ5 [17] values (Table 2) of 0.07, 0.27 and 0.21, respectively.

Although in **2** a value for that parameter is shown (Table 2) the relative orientation of one of the acetate anions and consequent proximity of the O-atom [Cu2···O4 bond distance of 2.902(2) Å] may lead to a six-coordinate copper complex; in such a situation, the Cu environment will be defined as N_1O_3 in the equatorial plan and two N-atoms of the chelating ligand in the axial sites. Such interaction appears to increase the global electron-donor ability of the ligand (decrease of the E_L parameter; see below, electrochemistry section).

In what concerns **3**, it consists of two complexes, a mononuclear and a dinuclear one. While Cu1 stands in a square pyramid environment and belongs to a monomeric complex, the coordination sphere of the Cu2 atom discloses an octahedron resulting from the long range Cu2···Cl4 interaction [3.1710(8) Å] with a symmetry generated Cu2 moiety, leading to a dimeric complex with an inversion centre in the middle of a Cu_2Cl_2 core.

An interesting feature of **2** – **6** concerns the angle (denoted as angle *A*) between the terpyridine plane (defined by the N atoms) and that of the attached phenyl group. In none of the complexes these two assemblies are co-planar and the twisting of the phenyl rings relative to the terpyridine planes assume values from 16.82º (in **4**) to 31.12º (in the Cu1 molecule of **3**).

The disparity of the Cu–N bond distances, the one involving the central nitrogen atom being shorter than those concerning the terminal N-atoms (Table 2), is usual and results from chelating ligand constrains. However, this trend is not followed in complex **6** where the latter is *ca*. 0.03 Å shorter than the former; moreover, in this complex the Cu–N bond length is the shortest one found in the series of compounds of this work. Also in **6** the Cu–Cl distance is shorter than those in **3**.

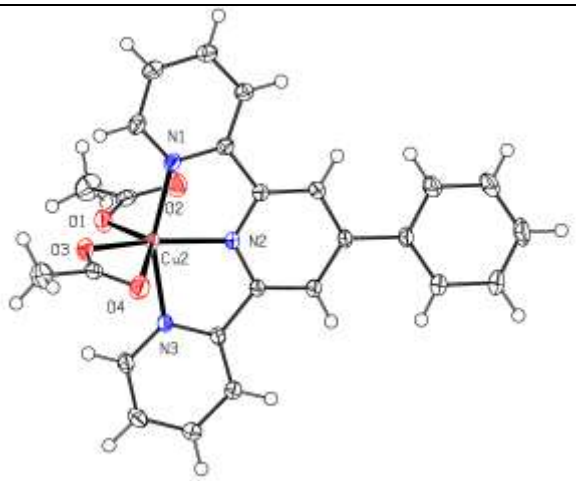
The interplanar distances of successive terpyridine moieties (shortest values found ranging from 3.5454(9) to 3.843(3) Å, see Table 2) suggested possible π-π interactions in all of the compounds. Moreover, in **3** and **5** very strong interactions between a metallacycle and a terpyridine ring of a

vicinal molecule were detected which, for the former, reached values as short as 2.964 Å. Although a long range Cu···Cl interaction has been detected for the Cu2-containing molecule in **3** and which led to dimerization (see above) the Cu···Cu separation in this complex [4.0131(6) Å] is shorter than that found for **6** [3.4031(8) Å]; in the other cases, such contacts exceed 7 Å.

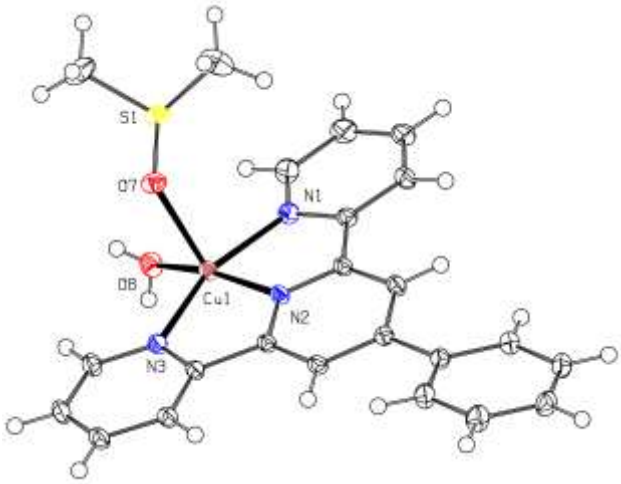
Table 1. Crystal data and structure refinement details for **2** − **6**.

	2	**3**	**4**	**5**	**6**
Formula unit	$C_{26}H_{23}Cl_2CuN_3O_4$	$C_{84}H_{60}Cl_8Cu_4N_{12}$	$C_{23}H_{23}CuN_5O_8S$	$C_{23}H_{22}CuN_4O_5$	$C_{22}H_{15}ClCuF_3N_3O_3$ S
Formula weight /g mol^{-1}	575.91	1775.20	593.06	497.98	557.42
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
T (K)	150(2)	150(2)	150(2)	296(2)	150(2)
Space group	*P*-1	*P*-1	*P*-1	P 21/n	P 21/c
a, Å	8.0783(3)	9.7921(8)	9.9081(4)	8.6645(5)	7.5816(15)
b, Å	11.2416(3)	13.3622(5)	10.6163(3)	24.9251(2)	12.192(2)
c, Å	14.5084(5)	15.6530(3)	13.7652(5)	9.9251(3)	20.344(4)
α, deg	76.347(2)	102.603(2)	101.172(2)	90.00	90.00
β, deg	89.396(3)	93.497(3)	101.232(2)	103.888(3)	90.60(3)
γ, deg	76.328(2)	104.137(2)	116.680(3)	90.00	90.00
Z	2	1	2	4	4
Volume , Å3	1242.61(7)	1924.03(18)	1201.88(9)	2080.80(14)	1880.4(6)
D_c, g cm^{-3}	1.539	1.532	1.639	1.590	1.969
μ(Mo Kα), mm^{-1}	1.133	1.423	1.056	1.096	1.481
Rfls. collected	29287	27787	15087	25187	9285
Rfls. Unique/observed	29287/6545	7025/5845	4436/ 4143	5201/4536	3299/ 2767
R_{int}	0.0251	0.0350	0.0282	0.0225	0.0883
Final $R1$ [a], $wR2$ [b] ($I \geq 2\,\sigma$)	0.0514, 0.1371	0.0324, 0.0821	0.0289, 0.0757	0.0466, 0.1399	0.0414, 0.1110
GOF on F^2	1.156	1.059	1.069	1.155	1.056

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$



(**2**)



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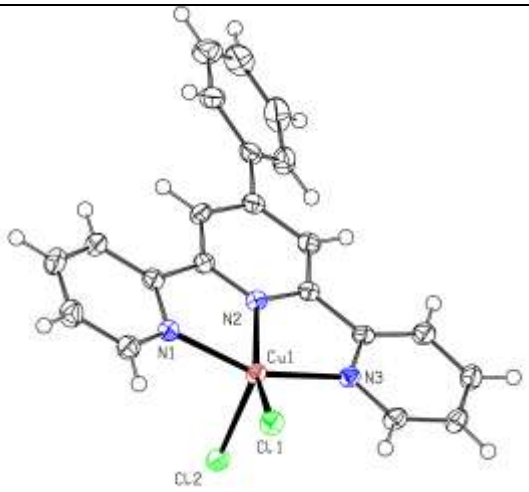
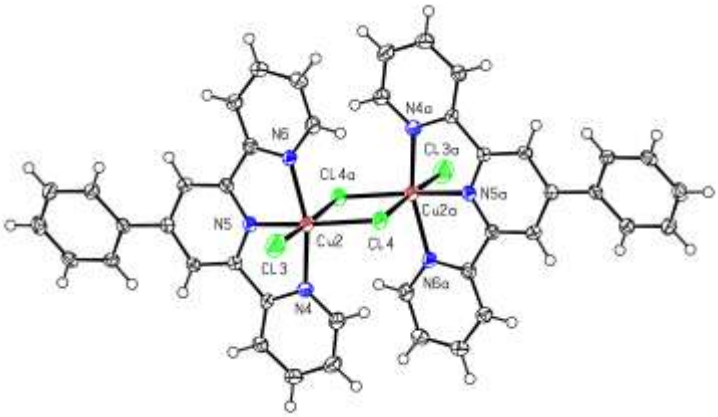
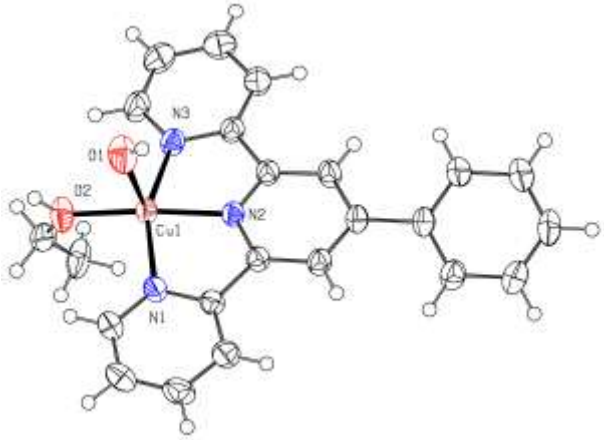
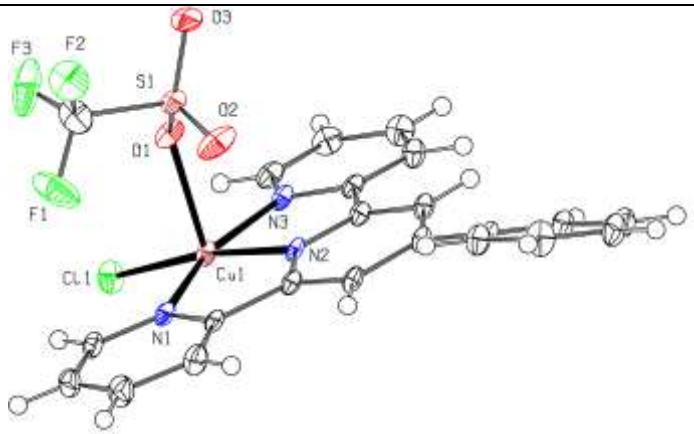


(**3**)





(**5**)



(**6**)

Figure 1. X-ray molecular structures of complexes **2** – **6** with partial atom numbering schemes. Ellipsoids are drawn at 50% probability. Dichloromethane of crystallization (in **2**) and nitrate counter ions (in **4** and **5**) were omitted for clarity. Symmetry operation to generate equivalent atoms (in **3**): *a*): 1-x,1-y,2-z.

Table 2 - Selected bond distances (Å) and angles (º) for complexes **2** – **6**.

Parameter	**2**	**3**	**4**	**5**	**6**
Equatorial environment	N_3O	N_3Cl	N_3O	N_3O	N_3Cl
Axial atom	$O_{acetate}$	Cl	O_{dmso}	$O_{hydroxide}$	$O_{sulfonate}$
τ_5	0.02	0.00	0.07	0.27	0.21
$Cu–N_{central\ pyridil}$	1.946(2)	1.958(2) (Cu1) 1.939(2) (Cu2)	1.9293(16)	1.935(3)	1.947(3)
$Cu–N_{terminal\ pyridils}$ (*avg.*)	2.029(2)	2.037(2)	2.034(16)	2.043(3)	1.919(2)
$Cu–Cl_{equatorial}$	-	2.2469(7) (Cu1) 2.2343(7) (Cu2)	-	-	2.2194(12)
$Cu–Cl_{axial}$	-	2.4410(7) (Cu1) 2.6570(9) (Cu2)	-	-	-
$Cu–O_{equatorial}$ $Cu–O_{axial}$	1.951(2) 2.114(2)	- -	1.9408(15) 2.2054(14)	1.913(3) 2.149(3)	- 2.197(2)
N–Cu–N (*minimum*) N–Cu–N (*maximum*)	79.62(9) 157.79(9)	78.67(8) 158.40(9)	79.54(7) 159.19(7)	79.32(12) 156.98(13)	79.21(11) 158.35(12)
Angle *A* [(i)]	28.46	31.12 (Cu1) 19.25 (Cu2)	16.82	20.75	24.37
Cu···mean basal plane N_3X (X = Cl or O)	0.312	0.352 0.207	0.217	0.148	0.123
Interplanar distances [(ii)]	3.5816(18)	3.6535(16)	3.5454(9)	3.843(3)	3.7025(18)

(i) Angle between the terpyridine and the attached phenyl planes (see text).

(ii) Involving only rings of the terpyridine ligands.

2.3. Electrochemical behaviour

Complexes **1**-**6** exhibit, by cyclic voltammetry (CV), at a platinum electrode at 25 ºC in a 0.2 M [^{n}Bu$_4$N][BF$_4$]/DMSO solution, two single-electron (as measured by controlled potential electrolysis) irreversible reduction waves, the former at potential values (Table 3) in the –0.06 to –0.48 V *vs*. SCE range, assigned to the Cu(II) → Cu(I) reduction (wave $\mathbf{I}^{\mathbf{red}}$), and the latter in the –1.23 to –1.58 V *vs*. SCE range assigned to the Cu(I) → Cu(0) process (wave $\mathbf{II}^{\mathbf{red}}$). Upon scan reversal, after the second cathodic process, an irreversible anodic wave ($\mathbf{I}^{\mathbf{ox}}$) at 0.05 – 0.16 V *vs*. SCE (Table 3) is observed, corresponding to the oxidation of cathodically generated (at the reduction level of wave $\mathbf{II}^{\mathbf{red}}$) Cu(0) species. Expectedly, no anodic waves have been detected for any of the complexes. A typical cyclic voltammogram is exemplified in Figure 2.

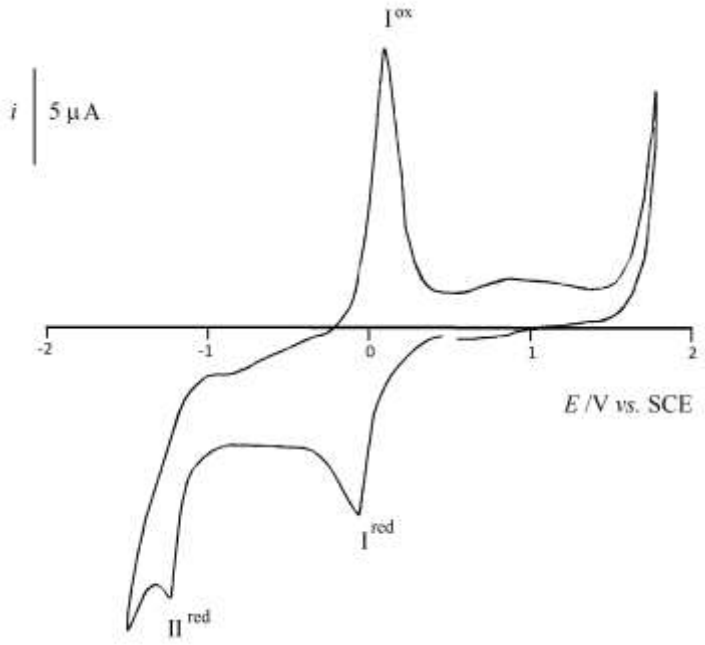


Figure 2 - Cyclic voltammogram of **4** in a 0.2 M [^{n}Bu$_4$N][BF$_4$]/DMSO solution, at a Pt disc working electrode (d = 0.5 mm), run at a scan rate of 200 mVs^{-1}.

The reduction potential of the complexes should reflect the relative electron donor/acceptor abilities of the ligands [18]. Lever [18d-f] developed an electrochemical parameterization approach,

expressed by the equation $E = S_M \times (\Sigma E_L) + I_M$, in which the redox potential of a complex (E) is related with electrochemical parameters determined by ligand and metal centre properties; ΣE_L is the sum of the values of the E_L ligand parameter for all the ligands (additive effect), S_M and I_M depend upon the metal and redox couple, the spin sate and stereochemistry. Such an approach was initially applied to octahedral-type complexes [18d-f], but subsequently extended to square-planar 16-electron and square-pyramid 18-electron complexes [19], as well as to half-sandwich type complexes [18a], but has never been applied to copper(II) centres. Indeed, the S_M and I_M values for the Cu(II)/Cu(I) redox couple are not known. Additionally, the E_L ligand parameter for the chelating 4,4'-terpyridine ligand is still not available, but since the Cu(II)-L core is common to complexes **1**-**6**, the variability in the redox potential should be mainly dependent on the co-ligands, *i.e.*, on the sum of their E_L values (ΣE_L of the co-ligands). However, only the complexes with the same stereochemistry are expected to follow the above Lever equation, with constant S_M and I_M values. Hence, only complexes **3** – **6** are directly comparable. The dinuclear form in the mixture **3** possibly dissociates to the mononuclear one in the electrolyte medium, since only single I^{red} and II^{red} reduction waves are observed. Alternatively, both complexes in **3** exhibit the same reduction potential what does not invalidate the discussion below.

Complexes **1** and **2** are expected to display a different stereochemistry since the acetate and nitrate ligands can chelate (see the above X-ray diffraction analysis of **2**) resulting into a higher Cu coordination number. In accord, a linear relationship between E_p (I^{red}) and ΣE_L of the co-ligands is observed for the closely related compounds **3** – **6** (Fig. 3). Nevertheless, one should be cautious since the reduction potentials are not the thermodynamic ones in view of the irreversible character of the reduction waves. However, such an approach can be valid for a series of closely related complexes and has been applied in other cases.[19]

Table 3. Cyclic voltammetric data[a] for $[Cu(NO_3)_2L]$ (**1**), **[**$Cu(OCOCH_3)_2L]\cdot CH_2Cl_2$ (**2**$\cdot CH_2Cl_2$), $[CuCl_2L].[Cu(Cl)(\mu\text{-}Cl)L]_2$ (**3**), $[Cu(H_2O)\{OS(CH_3)_2\}L](NO_3)_2$ (**4**)**,** $[Cu(HO)(CH_3CH_2OH)L](NO_3)$ (**5**) and $[CuCl(SO_3CF_3)L]$ (**6**)

Complex	E_p (I^{red})	E_p (II^{red})	E_p (I^{ox})[b]	ΣE_L (co-ligands)[c]
1	-0.29	-1.33	0.11	-0.22
2	-0.48	-1.43	0.13	-0.48
3	-0.23	-1.42	0.16	-0.48
4	-0.06	-1.23	0.07	+0.51
5	-0.27	-1.58	0.05	*ca*. -0.55
6	-0.21	-1.36	0.11	-0.37

[a] Potential values in Volt ± 0.02 *vs.* SCE, in a 0.2 M $[Bu_4N][BF_4]$/DMSO solution, at a Pt disc working electrode determined by using the $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ redox couple ($E_{1/2}^{ox}$ = 0.44 V *vs.* SCE [23]) as internal standard at a scan rate of 200 mVs^{-1}.

[b] Anodic wave generated upon scan reversal following the second reduction wave.

[c] Values in Volt *vs.* NHE, refer only to the ligands other than 4'-phenyl-terpyridine. E_L values for Cl^- (-0.24 V), $OSO_2CF_3^-$ (-0.13 V), NO_3^- (-0.11 V), OH^- (-0.59 V), water (0.04 V) and DMSO-*O* (0.47 V) have been indicated in the original publications [18d-f], and that of CH_3COO^- (-0.24 V) was proposed later [20].

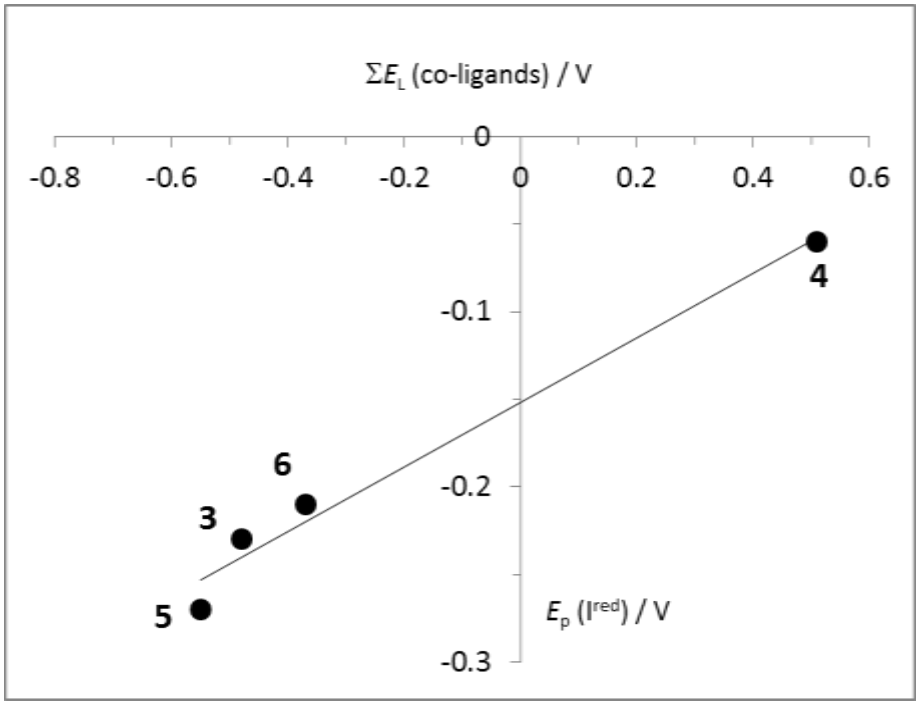
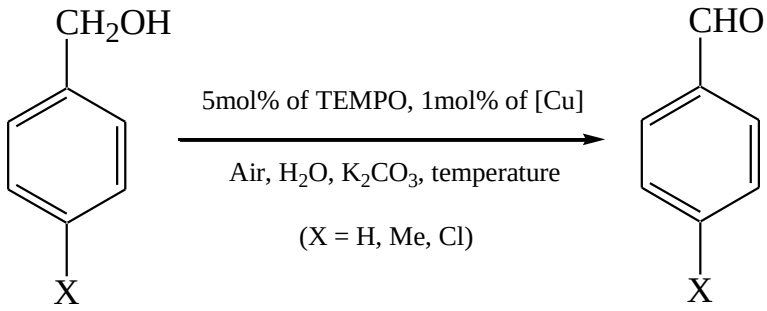


Figure 3 – Plot of the redox potential values for the first cathodic wave [E_p (I^{red})] *vs.* the sum of E_L ligand parameters of the co-ligands [ΣE_L of the co-ligands] for the 4'-phenyl-terpyridine complexes $[CuCl_2L].[Cu(Cl)(\mu\text{-}Cl)L]_2$ (**3**), $[Cu(H_2O)\{OS(CH_3)_2\}L](NO_3)_2$ (**4**), $[Cu(HO)(CH_3CH_2OH)L](NO_3)$ (**5**) and $[CuCl(SO_3CF_3)L]$ (**6**).

2.4. Catalytic aerobic oxidation of alcohols

The copper(II) complexes **1-6** catalyse the aerobic oxidation of benzyl alcohol, in alkaline (1 M K_2CO_3) aqueous solution and in the presence of the TEMPO (2,2,6,6-tetramethyl-piperidinyloxyl) radical, to the corresponding aldehyde. The formation of the aldehyde is predominant (yields up to 94 %, moles of product per mole of substrate), the lack of the corresponding carboxylic acid product conceivably being due to the well-known propensity of TEMPO for scavenging free radicals, thereby acting as an effective radical trap, avoiding the autoxidation [3e].



Scheme 2. Aerobic oxidation of benzylic alcohols in water.

The aerobic oxidation of benzyl alcohol (1.5 mmol) in alkaline (1 M K_2CO_3) aqueous solution, in the presence of a catalytic amount of the complex **1** (0.015 mmol, 1 mol % based on substrate) and TEMPO (0.075 mmol, 5 mol % based on substrate) resulted in a yield of 46 % on benzaldehyde after 6 h of reaction (Table 4, entry 5). Prolongation of the reaction time to 22 h induced a very good yield on this product (93 %; Table 4, entry 2). Reaction performed under the same conditions but with copper(II) nitrate resulted in only 2 % of benzaldehyde (Table 4, entry 22). The presence of TEMPO radical was confirmed to be crucial, since practically no oxidation of benzyl alcohol was observed in the absence of this radical (2 % yield; Table 4, entry 12).

We have also tested the influence of the amount of catalyst precursor on the oxidation of the alcohol (Figure 4). In the presence of **1**, similar yields of benzaldehyde (93-94 %; Table 4, entries 1-3) were observed for the substrate/catalyst (S/C) molar ratio from 70/1 to 200/1, but the TON improved from 72 to 186. Subsequent increase of the S/C ratio to 400 (decrease of the catalyst amount) resulted in a decrease of the yield to 80 % but a TON rising to 320 (Table 4, entry 4), on account of the slowing down of the reaction upon lowering the catalyst concentration.

Attempts to perform the aerobic oxidation of benzyl alcohol at temperatures lower than 70 ºC resulted in yield reductions (Figure 5, entries 6 and 7). For temperatures higher than that value, the yield decrease conceivably results from the lower solubility of oxygen in the reaction solution (Figure 5, entry 8).

The presence of base (K_2CO_3) was found to be crucial (its absence led to very low yield: 6%, Table 4, entry 9) and its amount was also optimized (Figure 6, entries 10 and 11).

Complex **1** proved to be the most active catalyst under the conditions of this study. Using complexes **2** – **6** as catalyst precursors and under the same conditions resulted also in high selectivities on the benzaldehyde, but yields in the 57 – 87 % range and TONs not higher than 87 (Table 4, entries 13 – 17).

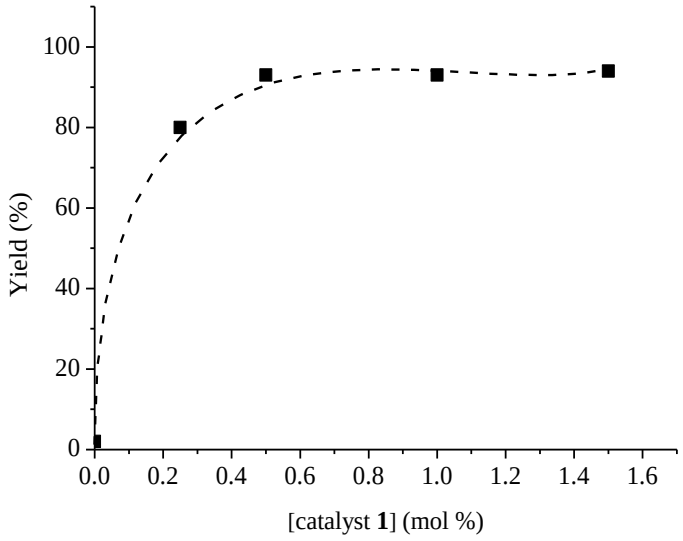


Figure 4 – Effect of catalyst precursor **1** amount (mol % *vs.* substrate) on benzaldehyde yield in the aerobic oxidation of benzyl alcohol. Reaction conditions: substrate (1.5 mmol), 0.075 mmol of TEMPO in 5 mL of 1M K_2CO_3 aqueous solution, 22 h.

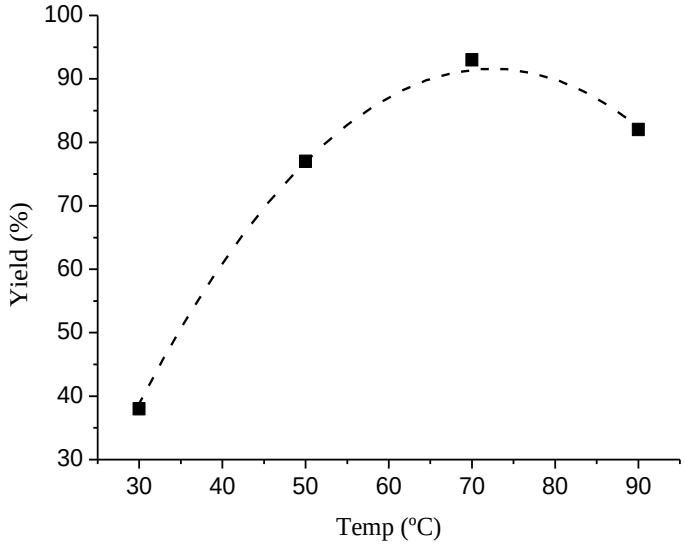


Figure 5 – Effect of the temperature on benzaldehyde yield (mol %, *vs.* substrate) in the aerobic oxidation of benzyl alcohol, catalyzed by **1**. Reaction conditions: substrate (1.5 mmol), 0.015 mmol of catalyst precursor and 0.075 mmol of TEMPO in 5 mL of 1M K_2CO_3 aqueous solution, 22 h.

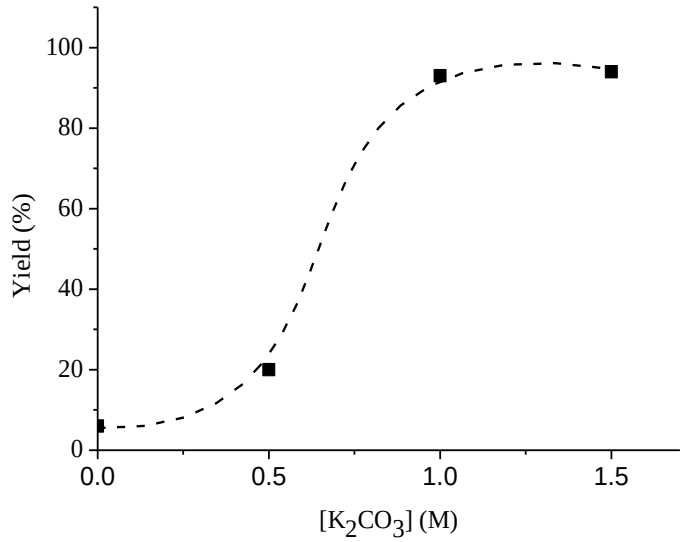


Figure 6 – Yield of benzaldehyde *vs.* concentration of K_2CO_3. Reaction conditions: substrate (1.5 mmol), 0.015 mmol of catalyst precursor and 0.075 mmol of TEMPO in different K_2CO_3 aqueous solution, 70 ºC, 22 h, 1 atm, air.

As it was shown before [9], substituted benzylic alcohols can also be converted to the corresponding aldehydes with moderate to good yields (Table 4, entries 18 and 19), while the oxidation of an aliphatic (1-hexanol, entry 20) or secondary benzylic alcohol (1-phenylethanol, entry 21) practically does not proceed, as also reported for other Cu/TEMPO catalysts [6g,10a,12b]. Our catalytic systems are expected [3a,12a-12c] to involve the coordination (with deprotonation) of benzyl alcohol ($PhCH_2OH$) and TEMPO radical to the copper centre, followed by hydrogen abstraction from the former to the latter with resulting formation of the *O*-ligated radical $PhHC^{\bullet}\text{-}O^{-}$ and TEMPOH. Intramolecular electron-transfer from ligated $PhHC^{\bullet}\text{-}O^{-}$ to Cu^{II} leads to the formation of the aldehyde PhCHO and Cu^{I} which is reoxidized to Cu^{II} by dioxygen. The TEMPO radical is also regenerated upon oxidation of TEMPOH.

Table 4. Aerobic oxidation of selected alcohols to the corresponding carbonyl compounds[a]

Run	Complex	$\frac{\text{Substrate}}{\text{Complex}}$	Substrate	Product	Yield [b] [%]	TON
1	**1**	70/1	Benzyl alcohol	Benzaldehyde	94	72
2	**1**	100/1	Benzyl alcohol	Benzaldehyde	93	93
3	**1**	200/1	Benzyl alcohol	Benzaldehyde	93	186
4	**1**	400/1	Benzyl alcohol	Benzaldehyde	80	320
5[c]	**1**	200/1	Benzyl alcohol	Benzaldehyde	46	92
6[d]	**1**	100/1	Benzyl alcohol	Benzaldehyde	38	38
7[e]	**1**	100/1	Benzyl alcohol	Benzaldehyde	77	77
8[f]	**1**	100/1	Benzyl alcohol	Benzaldehyde	82	82
9[g]	**1**	100/1	Benzyl alcohol	Benzaldehyde	6	6
10[h]	**1**	100/1	Benzyl alcohol	Benzaldehyde	20	20
11[i]	**1**	100/1	Benzyl alcohol	Benzaldehyde	94	94

12[j]	**1**	100/1	Benzyl alcohol	Benzaldehyde	2	2
13	**2**	100/1	Benzyl alcohol	Benzaldehyde	60	60
14	**3**	100/1	Benzyl alcohol	Benzaldehyde	75	75
15	**4**	100/1	Benzyl alcohol	Benzaldehyde	57	57
16	**5**	100/1	Benzyl alcohol	Benzaldehyde	87	87
17	**6**	100/1	Benzyl alcohol	Benzaldehyde	67	67
18	**1**	200/1	4-Me-benzyl alcohol	4-Me-benzaldehyde	78	156
19	**1**	200/1	4-Cl-benzyl alcohol	4-Cl-benzaldehyde	47	94
20	**1**	200/1	1-Hexanol	Hexanal	0	0
21	**1**	200/1	1-Phenylethanol	Acetophenone	<1	<2
22	$Cu(NO_3)_2$	200/1	Benzyl alcohol	Benzaldehyde	2	4

[a] Conditions, unless stated otherwise: 1.5 mmol of the substrate, 0.015mmol (1 mol%) of catalyst precursor and 0.075mmol (5 mol%) of TEMPO in 5mL of 1M K_2CO_3 aqueous solution, 1 atm. air, 22 h. [b] Yields based on GC analyses, selectivity in all cases >99 %. [c] 6 h. [d] 30ºC. [e] 50ºC. [f] 90ºC. [g] Reaction without K_2CO_3. [h] 0.5 M K_2CO_3. [i] 1.5 M K_2CO_3. [j] Reaction without TEMPO.

3. Conclusions

We have synthesized a number of copper(II) complexes with 4'-phenyl-terpyridine ligand and found that they act as active catalyst precursors for the aerobic oxidation of alcohols, under mild conditions and in the presence of TEMPO radical. The effects of various parameters have been investigated and allowed us to achieve yields and TONs of *ca*. 94% and 320, respectively. The most active catalyst for the optimized conditions is complex **1** with nitrate ligands.

This study also indicates that the copper(II) complexes may exhibit redox potential-structure relationships, based on the electrochemical Lever E_L ligand parameter, that are similar to those already established for closed-shell octahedral-type complexes, 16-electron square-planar and 18-

electron square-pyramid transition metal d^8 complexes, and half-sandwich complexes, what constitutes a promising and still unexplored subject which deserves further investigation.

4. Experimental

X-ray Diffraction Analysis

The X-ray diffraction data of **2**-**6** were collected using a Bruker AXS-KAPPA APEX II diffractometer with graphite monochromated Mo-Kα radiation. Data were collected using omega scans of 0.5º per frame, and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART [24a] software and refined using Bruker SAINT [24a] on all the observed reflections. Absorption corrections were applied using SADABS [24a]. Structures were solved by direct methods using the SHELXS–97 [24b] package and refined with SHELXL-97 [24b]. All hydrogen atoms were inserted in calculated positions, except those of coordinated water molecule (H8A and H8B) in **4**, and the hydroxide (H1A) and methoxide (H2A) in **5**, which were located in the difference Fourier map and included in the refinement using the riding-model approximation with coefficients 1.5 times larger than the respective parameters of the parent atoms. There were disordered molecules present in the structure of complex **3**. Since no obvious major site occupations were found for those molecules, it was not possible to model them. PLATON/SQUEEZE [24d] was used to correct the data and potential volumes of 152 $Å^3$ were found with 41 electrons per unit cells worth of scattering. These were removed from the models and not included in the empirical formula. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for most of the remaining atoms were employed.

CCDC 967358 (**2**) - 967362 (**6**) contain the supplementary crystallographic data for this paper. Crystallographic details and selected structural dimensions are listed in Tables 1 and 2 respectively.

4.1 Instrumentation and Reagents

All reagents were of analytical grade or purified by standard methods. 4'-phenyl-terpy (L) was prepared by following a reported procedure [22].

IR spectra were measured with a Perkin–Elmer Spectrum 2000 or a Magna 750 FT-IR spectrophotometer, in KBr pellets (wavenumbers in cm^{-1}; abbreviations: *vs*, very strong; *s*, strong; *m*, medium; *w*, weak; *br*, broad). The UV-Vis absorption spectra of DMSO and water solutions of **1-6** in 1.00 cm quartz cells, were recorded at room temperature on a Lambda 35 UV-Vis spectrophotometer (Perkin-Elmer) by scanning the 200 – 800 nm region at a rate of 240 nm min^{-1}. Electrospray mass spectra (ESI-MS) were recorded on a Finnigan LCQ Mass Spectrometer using dimethylformamide-methanol as the mobile phase.

C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. The electrochemical experiments were performed on an EG&G PAR 273A potentiostat/galvanostat connected to a personal computer through a GPIB interface. Cyclic voltammetry (CV) studies were undertaken in 0.2 M $[^{n}Bu_4N][BF_4]$/DMSO, at a platinum disc working electrode (d = 0.5 mm) and at room temperature. Controlled-potential electrolyzes (CPE) were carried out in electrolyte solutions with the above-mentioned composition, in a three-electrode H-type cell. The compartments were separated by a sintered glass frit and equipped with platinum gauze working and counter electrodes. For both CV and CPE experiments, a Luggin capillary connected to a silver wire pseudo-reference electrode was used to control the working electrode potential. A Pt wire was employed as the counter-electrode for the CV cell. The CPE experiments were monitored regularly by cyclic voltammetry, thus assuring no significant potential drift occurred along the electrolysis. The solutions were saturated with N_2 by bubbling this gas before each run, and the redox potentials of the complexes were measured by CV in the presence of ferrocene as the internal standard, and their values are quoted relative to the SCE by using the $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$

redox couple ($E^{ox}_{1/2}$ = 0.44 V *vs.* SCE) [23]. Gas chromatographic (GC) measurements were carried out using a FISONS Instruments GC 8000 series gas chromatograph with a FID detector and a capillary column (DB-WAX, column length: 30 m; internal diameter: 0.32 mm). The temperature of injection was 240 ºC. The initial temperature was maintained at 120 ºC for 1 min, then raised 10 ºC/min up to 200 ºC, and held at this temperature for 1 min. Helium was used as the carrier gas.

4.2 Syntheses

4.2.1 [$Cu(NO_3)_2L$] (1)

$Cu(NO_3)_2 \cdot 2.5H_2O$ (0.240 g, 1.0 mmol) was dissolved in 20 mL acetonitrile and 20 mL of a dichloromethane solution of L (0.247g, 0.80 mmol) was added dropwise during half an hour and stirred for 24 h. The mixture was then filtered to isolate a blue solid which was washed with small portions of dichloromethane, acetonitrile and finally with methanol (0.347 g, 84 % yield). Anal. Calcd for $C_{21}H_{15}CuN_5O_6 \cdot H_2O$ (514.9): calcd. C 49.0, H 3.3, N 13.6; found C 49.1, H 3.2, N 13.7. MS: $[M - 2NO_3 - H^+]^+$: (372, 100%), $[M - NO_3)]^+$ (434, 35%). IR (KBr disk) ν (cm^{-1}): 1615 (*vs*, $_{pyridyl\text{-}H}$), 1557 (*s*, $\nu_{aryl\text{-}H}$), 1503 (*vs*, $\nu_{pyridyl\text{-}H}$), 1421 (*m*, $\nu_{pyridyl\text{-}H}$), 1163 (*m*), 1098 (*m*, $\nu_{N\text{-}O}$), 1023 (*vs*), 974 (*m*, $\delta_{Ar\text{-}H}$). λ_{max} (DMSO)/ nm 297 (ε/ M^{-1} cm^{-1} 2974), 658 (313); λ_{max} (H_2O)/ nm 294 (ε/ M^{-1} cm^{-1} 1374), 655 (384). Blue crystals of **1** were obtained upon diffusion of diethyl ether to a DMF solution of the complex, but they were not suitable for X-ray analysis.

4.2.2. [$Cu(OCOCH_3)_2L] \cdot CH_2Cl_2$ ($2 \cdot CH_2Cl_2$)

20 mL of a dichloromethane solution of L (0.155 g, 0.501 mmol) was added dropwise to 20 mL of a methanol solution of $Cu(CH_3COO)_2 \cdot H_2O$ (0.100 g, 0.501 mmol) and the mixture was stirred for 24 h. Diethyl ether was then allowed to diffuse into the solution leading to the formation of green crystals of **2** (0.216 g, 85% yield), which were suitable for X-ray analysis. Anal. Calcd for $C_{25}H_{21}CuN_3O_4 \cdot CH_2Cl_2$ (575.9): calcd. C 54.2, H 4.0, N 7.3; Found: C 54.4, H 4.2, N 7.0. IR (KBr disc) (cm^{-1}): 3420 (*br*, s, ν_{OH}), 3059 (*w*), 2924 (*w*, νCH_3), 1574 (*vs*, *br*, $\nu_{C=O}$, $\nu_{pyridyl\text{-}H}$), 1475 (*s*, $\nu_{pyridyl\text{-}H}$), 1416 (*vs*, $\nu_{pyridyl\text{-}H}$), 1333 (*m*), 1248 (*m*), 1163 (*w*), 1021 (*m*), 898 (*w*, $\delta_{Ar\text{-}H}$), 794 (*m*, $\delta_{Ar\text{-}H}$), 768 (*s*, $\delta_{Ar\text{-}H}$), 730 (*m*), 684 (*s*), 657 (*m*), 628 (*w*). λ_{max} (DMSO)/ nm 317 (ε/ M^{-1} cm^{-1} 2949), 673 (124); λ_{max} (H_2O)/ nm 315 (ε/ M^{-1} cm^{-1} 2937), 670 (101).

4.2.3 $[CuCl_2L].[Cu(Cl)(\mu\text{-}Cl)L]_2$ (3)

$CuCl_2$ (0.312 g, 2.32 mmol) was dissolved in 20 mL methanol and 20 mL of a dichloromethane solution of L (0.619 g, 2.00 mmol) was added dropwise. The mixture was then stirred for 24 h after which the green solid was isolated by filtration and washed with methanol (2 × 10 mL), then with dichloromethane (2 × 10 mL) and dried under vacuum (0.656 g, 57 %). Anal. Calcd for $C_{21}H_{15}Cl_2Cu_1N_3{\cdot}0.5H_2O{\cdot}0.5CH_2Cl_2$ (495.3): calcd. C 52.1, H 3.5, N 8.5; found C 51.8, H 3.5, N 8.5. IR (KBr disk) ν (cm^{-1}): 1609 (*vs*, $\nu_{pyridyl\text{-}H}$), 1558 (*s*, $\nu_{aryl\text{-}H}$), 1476 (*vs*, $\nu_{pyridyl\text{-}H}$), 1417 (*vs*), 1248 (*m*), 1164 (*m*), 1102 (*w*), 1020(*vs*), 898 (*m*). λ_{max} (DMSO)/ nm 292 (ε/ M^{-1} cm^{-1} 31683), 736 (290); λ_{max} (H_2O)/ nm 287 (ε/ M^{-1} cm^{-1} 28986), 680 (225). Green crystals of **3** suitable for X-ray analysis were obtained by dissolving the complex in a 1:1 mixture of methanol and dichloromethane followed by slow evaporation at room temperature.

4.2.4. $[Cu(H_2O)\{OS(CH_3)_2\}L](NO_3)_2$ (4)

Compound **1** (0.10 g, 0.19 mmol) was dissolved in 20 mL of a 1:9 combination of DMSO and methanol and heated at 60 °C for 2 h. Upon very slow diffusion of diethyl ether to the reaction mixture, blue crystals were obtained (0.059 g, 51 %), which were suitable for X-ray determination. Anal. Calcd for $C_{23}H_{23}CuN_5O_8S$ (593.1): C 46.6, H 3.9, N 11.8; found: C 46.4, H 4.2, N 12.0. IR (KBr disc) (cm^{-1}): 3404 (*br*, *m*, ν_{OH}), 3056 (*w*), 3013 (*w*), 1763 (*m*), 1608 (*vs*, $\nu_{pyridyl\text{-}H}$), 1557 (*s*), 1476 (*s*, $\nu_{pyridyl\text{-}H}$), 1418 (*vs*, br, $\nu_{pyridyl\text{-}H}$), 1305 (*w*), 1246 (*m*), 1161 (*m*), 1105 (*w*), 1019 (*s*), 950 (*m*), 894 (*m*, $\delta_{Ar\text{-}H}$), 825 (*s*), 794 (*s*, $\delta_{Ar\text{-}H}$), 768 (*s*, $\delta_{Ar\text{-}H}$), 728 (*m*), 687 (*m*), 646 (*m*), 627 (*m*). λ_{max} (DMSO)/ nm 301 (ε/ M^{-1} cm^{-1} 3005), 698 (940); λ_{max} (H_2O)/ nm 306 (ε/ M^{-1} cm^{-1} 2692), 695 (890).

4.2.5. $[Cu(HO)(CH_3CH_2OH)L](NO_3)$ (5)

Compound **1** (0.18 g, 0.35 mmol) was dissolved in a 20 mL of a 1:1 combination of ethanol and DMF, and 2 mL of an ethanolic solution of 4,4'-bipyridyl (4,4'-Bpy) (0.0274 g, 0.18 mmol) was

added dropwise; this mixture was stirred for 24 h and then refluxed for 3 h, after which it was filtered and the mother solution allowed to evaporate naturally. Blue crystals (0.078 g, yield 45 % based on the precursor) were obtained, which were suitable for X-ray determination. Anal. Calcd for $C_{23}H_{22}CuN_4O_5$ (497.9). C: 55.5, H 4. 5, N 11.3.; found: C 55.8, H 4.7, N 11.1. IR (KBr disc) (cm^{-1}): 3403 (*br*, *m*, ν_{OH}), 3044 (s), 2774 (*w*), 1763 (*m*), 1608 (*vs*, $\nu_{pyridyl\text{-}H}$), 1559 (*s*), 1475 (*s*, $\nu_{pyridyl\text{-}H}$), 1385 (*s*), 1307 (*m*), 1244 (*m*), 1156 (*m*), 1076 (*w*), 1068 (*w*), 1044 (*w*), 1035 (*w*), 1018 (*s*), 984 (*m*), 926 (*m*), 894 (*m*, $\delta_{Ar\text{-}H}$), 851 (*s*), 825 (*m*), 802 (*m*), 765 (*s*, $\delta_{Ar\text{-}H}$), 729 (*m*), 692 (*m*), 683 (*m*), 656 (*m*), 646 (*m*), 626 (*m*), 615 (*m*). λ_{max} (DMSO)/ nm 319 (ε/ M^{-1} cm^{-1} 2789), 677 (480); λ_{max} (H_2O)/ nm 323 (ε/ M^{-1} cm^{-1} 2452), 674 (410).

4.2.6 [CuCl(SO_3CF_3)L] (6)

0.243 g (0.491 mmol) of compound **3** was dissolved in 75 mL of a 7:7:1 mixture of methanol, dichloromethane and DMF and 10 mL of an acetonitrile solution of $AgSO_3CF_3$ (0.129 g, 0.502 mmol) were added dropwise for a period of 30 minutes. The mixture was then stirred for 24 h, after which it was filtered and the mother solution allowed evaporating. Blue crystals of **6** (0.173 g, yield 63%) were obtained, which were suitable for X-ray analysis. Anal. Calcd for $C_{22}H_{15}ClCuF_3N_3O_3S$ (557.4): C 47.4, H 2.7, N 7.5; found C 47.4, H 2.6, N 7.5. IR (KBr disk) ν (cm^{-1}): 1614 (*vs*, $\nu_{pyridyl\text{-}H}$), 1564 (*s*, $\nu_{aryl\text{-}H}$), 1476 (*vs*, $\nu_{pyridyl\text{-}H}$), 1418 (*vs*), 1286 (*vs*), 1150 (*m*), 1026(*vs*), 891 (*m*). λ_{max} (DMSO)/ nm 291 (ε/ M^{-1} cm^{-1} 30547), 732 (1394); λ_{max} (H_2O)/ nm 287 (ε/ M^{-1} cm^{-1} 28986).

4.3. Catalytic Studies

The reactions were carried out according to published procedure [9]. Under typical conditions, they were performed in flasks fitted with water circulating condensers under atmospheric pressure of air. 1.5 mmol of the substrate, 0.015 mmol (1 mol % based on substrate) of Cu catalyst, 0.075 mmol (5

mol%) of TEMPO and 5 mL of 1M K_2CO_3 aqueous solution were added and the reaction mixture was stirred for 22 h at 70 ºC after which the addition of 1 M HCl (for neutralization) and 5 mL of EtOAc (for the extraction of the substrate and of the organic products from the reaction mixture) were accomplished. Finally, 120 μL of cycloheptanone (internal standard) were added. The products were analysed by GC and quantified by using the internal standard method.

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